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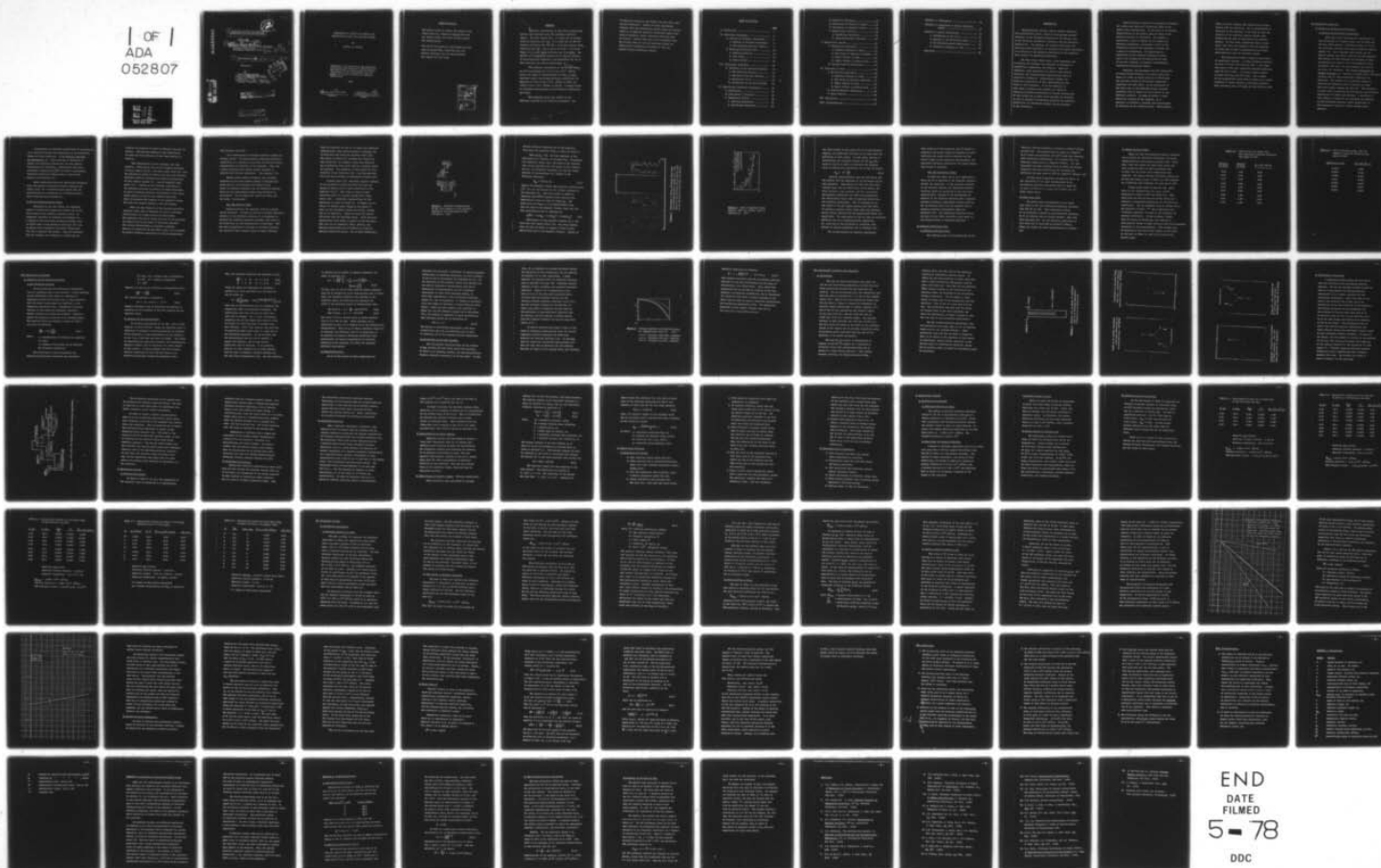
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MEASUREMENT OF CUPRIC AND ZINCATE ION DIFFUSIVITIES USING THE C--ETC(U)
MAR 74 J GENDLER, L NANIS, M LITT

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MEASUREMENT OF CUPRIC AND ZINCATE ION
DIFFUSIVITIES USING THE CAPILLARY METHOD.

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MEASUREMENT OF CUPRIC AND ZINCATE ION
DIFFUSIVITIES USING THE CAPILLARY METHOD

by

Jeffrey L. Gendler

Presented to the Faculty of the Department
of Chemical and Biochemical Engineering of
the University of Pennsylvania in partial
fulfillment of the requirements for the
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1976

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ABSTRACT

Diffusion coefficients of four binary electrolyte systems were measured using the capillary-reservoir method. The four systems are: 1.0 molar KCl in aqueous solution diffusing into H_2O ; 0.01 molar ZnO in 40% KOH solution diffusing into 40% KOH ; 0.05 molar aqueous $CuSO_4$ diffusing into H_2O ; and a series of 0.005 - 0.10 molar $CuSO_4$ in 0.5 molar H_2SO_4 diffusing into 0.5M H_2SO_4 . The ZnO/KOH and $CuSO_4/H_2SO_4$ systems are of current interest to electrochemical engineers, and demonstrate the use of this technique for binary electrolytes.

The diffusion coefficient of the ZnO/KOH system at 25°C was measured as $7.22 \pm 1.90 \times 10^{-6}$ cm²/sec. Across the range of concentrations of $CuSO_4$ in H_2SO_4 described above, the average diffusion coefficient was measured as $5.43 \pm 0.59 \times 10^{-6}$ cm²/sec at 25°C, and $6.675 \pm 0.97 \times 10^{-6}$ cm²/sec at 35.5°C. A slight effect of diffusant concentration on the diffusion coefficient was found.

The $CuSO_4/H_2O$ system was studied in two different versions of the capillary technique: one

in which the reservoir was stirred, and the other under no-stir conditions. Results of these experiments indicate that the hydrodynamic effect caused by stirring leads to an apparent diffusion coefficient higher than would be expected, unless sufficient diffusion time is allowed. Present data lead to the conclusion that the no-stir model is the most practical choice for obtaining the diffusion coefficient of this and similar binary electrolyte systems.

TABLE OF CONTENTS

	<u>Page</u>
I. Introduction	1
II. Historical Background	4
A. History of Diffusion Measurement	4
1. Methods of Diffusion Measurement	4
2. The Capillary-Reservoir Method ...	5
B. Existing Diffusivity Data	14
1. Potassium Chloride	14
2. Zinc Oxide	15
3. Cupric Sulfate	16
III. Theoretical Background	19
A. Solutions of the Diffusion Equation	19
1. The Diffusion Equation	19
2. Stirring of the Bulk Solution	20
3. Calculation of Δl	22
4. No-Stirring of the Bulk Solution	23
IV. Experimental Apparatus & Procedures	27
A. Capillaries	27
B. Flow-Channel / Reservoir	31
C. Temperature Control	33
1. Stirring Experiments	33
2. No-Stirring Experiments	34

D. Analytical Technique.....	35
E. Calculation of Capillary Volumes	36
F. Calculation of Reynold's Number	36
G. Experimental Procedure	38
1. No-Stirring Experiment	38
2. Stirred-Reservoir Experiment	40
V. Experimental Results	41
A. No-Stirring Experiments	41
1. Potassium Chloride in Water	41
2. Zinc Oxide in Potassium Hydroxide ...	41
3. Cupric Sulfate in Water	42
4. Cupric Sulfate in Sulfuric Acid	42
B. Stirred-Reservoir Experiments	43
VI. Discussion of Data	49
A. No-Stirring Experiments	49
1. Potassium Chloride in Water	49
2. Zinc Oxide in Potassium Hydroxide ...	50
3. Cupric Sulfate in Water	53
4. Cupric Sulfate in Sulfuric Acid	55
B. Stirred-Reservoir Experiments	61
C. Error Analysis	64
VII. Conclusions	69
VIII. Recommendations	72

APPENDIX A: Nomenclature	73
APPENDIX B: Calculation of Optimum Capillary Length	75
APPENDIX C: Sample Calculations	77
1. Calibration of the A.A.S.	77
2. Example of the No-Stirring Model	77
3. The Stirred-reservoir Experiments	79
4. Analysis of Variance of Data	80
References	82

INTRODUCTION

Electrochemical systems, such as electric batteries and electroplating tanks, cannot be well-designed without knowledge of the transport properties of the system, such as the diffusion coefficient, viscosity, and the electrical conductivity. For example, the relation which gives the limiting current density at an electrode in a given electrolyte is a function of the diffusion coefficient of the migrating ionic species in supporting electrolyte.

For many binary liquid pairs, fluid properties such as density and viscosity are tabulated as functions of composition, temperature, and pressure. Where not tabulated, these properties may often be very closely estimated with well-developed approximations found in scientific literature. Unfortunately, though, the diffusion coefficients of many electrolytes are not found in the literature. It is the intention of this study to explore some aspects of a method of measuring diffusion coefficients of aqueous electrolytes. If this method can be shown to be reliable and accurate, it will be possible to accurately determine the diffusion coefficients of electrolyte systems not yet discussed in the literature.

Most analytical techniques for measuring a property of a system are based on a theoretical model of the system under consideration. If the model is an accurate representation of the system, then the value of the measured property is believable. For example, a thermometer, which is thought of as a device for measuring temperature, represents a model of the relationship between the expansion of mercury and a change in temperature. By calibrating the thermometer at two standard (reference) points, such as the melting and boiling points of water at one atm. pressure, it becomes a standardized, reproducible measurement device.

Similarly, the techniques used for measurement of liquid-liquid diffusion in a binary system are based on a model of Fick's First Law of Diffusion. The capillary method of diffusivity measurement represents one such model. In the development of the model used in the capillary method, boundary conditions must be chosen for the solution of the diffusion equation. In order to obtain a simple analytical solution of the equation, it is necessary to maintain a constant zero-concentration of diffusant at the capillary mouth. Unfortunately,

doing so causes unwanted side effects due to fluid flowing past the capillary.' And if concentration of diffusant at the capillary is not kept at zero, the solution of the diffusion equation becomes very complicated and must be approximated by numerical methods.' In this study, experiments based on both models were done, and compared, with the intention of being able to make a recommendation for future experimentation with the capillary method.'

The electrolyte systems studied in this series of experiments include: 1.0 molar potassium chloride in water diffusing into water at 25°C. ; 0.01 molar zinc oxide in 40% (wt.) potassium hydroxide diffusing into 40% KOH at 25°C. ; 0.05 molar cupric sulfate in water diffusing into 26° water ; and a series of low-concentration (less than or equal to 0.1 molar) solutions of cupric sulfate in half-molar sulfuric acid, diffusing into 0.5M H₂SO₄ at both 25°C and 35°C.

II. Historical Background

A. History of Diffusivity Measurement

1. Methods of Diffusivity Measurement

There exist many techniques for measurement of the diffusivity in a binary system, all of which have the same basic pattern: Initially species "A" is in one container, isolated from another container holding species "B". For a measured time period, the two species contact each other, then the two are separated. The contents of each container are analyzed in order to determine how much "A" is in the container which originally held only "B", and likewise, how much "B" is in the "A" container. The textbook Techniques of Organic Chemistry (1) contains a chapter called "Diffusivity" in which many of these measurement techniques are discussed. For example, it is sometimes useful to have the two diffusion cells cylindrical in shape and allow contact through one open end. This technique is often used in measuring the diffusivity (the diffusion coefficient) of binary gas mixtures. A variation of this method, in which the two cylinders are separated by semi-permeable membrane, allows measurement of the transport of gases or liquids through such a membrane.

In measuring the diffusion coefficients of electrolytes, it is useful to measure the conductance of the electrolyte before and after diffusion. In The Physical Chemistry of Electrolytes (2) , this technique is developed in detail, and diffusion coefficients for many aqueous electrolytes are tabulated. Experimental data based on Harned's conductometric^{data} may be found in contemporary literature describing diffusivities of very dilute aqueous salt solutions (3) .

Other established diffusion measurement techniques used with aqueous electrolytes include measuring the weight change of a diffusant-filled porous disc (4) , and measuring the conductance of a diffusing system with a rotating disc electrode (5) .

2. The Capillary-Reservoir Method

Introduced in the late 1940's, the capillary method of diffusivity measurement remains one of the most versatile and reliable techniques in use. As originally described by Anderson and Saddinton (6) , a capillary tube with small diameter-to-length ratio is filled with a known amount of diffusant ("A") and is placed into a container (reservoir) filled with "B", for a measured time period. After the diffusion time has elapsed, the capillary is removed and its

contents are analyzed in order to determine how much "A" remains. Anderson and Saddington used radiotracers to study the self-diffusion of some ionic species in solution.

Many applications of this technique have been reported. Radiotracers were used in studying diffusion in liquid metals (7),(8) , and with molten salts (9), (10). The radiotracer method of analysis has been used with the capillary method in studying the diffusion coefficients of some organic liquids (11) , and of liquified inert gases (12) . Because of the intrinsic simplicity of the capillary-reservoir technique, it could conceivably be used to evaluate diffusion coefficients in any binary liquid system, as long as some method exists with which to determine the contents of the capillary before and after the allotted diffusion time has elapsed.

There are many features of the capillary-reservoir technique which make it desirable for use in measuring diffusivities of a large variety of liquid pairs. The apparatus need not be large; the size of the capillary is limited only by the amount of diffusant necessary for accurate determination of capillary contents. Because the system may be kept quite small, it is feasible to conduct diffusion experiments at extreme temperatures

and pressures (13),(14).

It is advantageous to minimize capillary length for another reason: the experimentally-determined diffusion coefficient is a function of the ratio of final-to-initial concentration of diffusant in the capillary. Thus, for a given diffusion time period, greater accuracy is possible with shorter capillaries. (See Appendix "B").

Despite these positive features, the capillary technique is not used commonly because of disagreement among users of the technique with regard to the choice of boundary conditions for the diffusion equation. There are two mathematical models being discussed by researchers: one is called the "stirring" model, and the other, "no-stirring".

(a). The Stirring Model

During diffusion, the capillary sits in a liquid filled reservoir. In order to achieve a complete analytical solution of the diffusion equation, it is necessary to maintain the capillary-reservoir interface (the mouth of the capillary) at zero-concentration of diffusant. This has been accomplished in the past by stirring (flowing) the reservoir fluid rapidly enough to remove diffusant

from the interface as soon as it leaves the capillary. Unfortunately, this stirring causes a "sweeping out" of diffusant from below the capillary mouth (15). The region in which this "sweeping out" occurs has been termed the " $\Delta \ell$ -region", since mass transport due to diffusion only occurs through a reduced length of capillary. The existence of this region has been confirmed in the laboratory (16) , and the magnitude of $\Delta \ell$ has been measured by photographic methods (15).

A recent paper (17) describes computer modeling of the streamlines associated with flow past the capillary mouth, so as to allow estimation of the magnitude of $\Delta \ell$. This model is based on work describing flow of a viscous liquid past a sharp corner (18). A pictorial representation of this phenomenon is shown in Figure 1a. In Figure 1b, the effect of viscous forces acting on the liquid is seen, as the streamlines become horizontal, leading out of the capillary. Figure 1c shows the overall $\Delta \ell$ -effect near the capillary mouth. Using potassium permanganate (deep purple in color) as the diffusant, and water in the reservoir, Nanis, Bockris, and Richards photographed the $\Delta \ell$ -effect in a stirred capillary-reservoir system. One of their photographs,

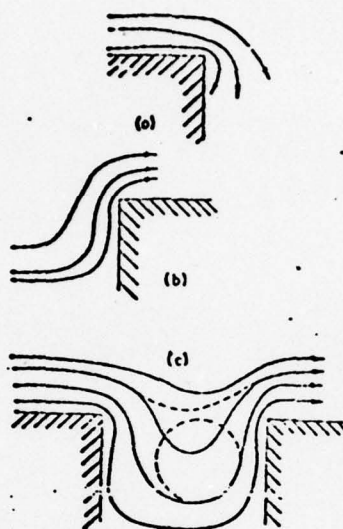


Figure 1. Schematic representation of the flow patterns in the capillary leading to the development of the Δl -region. (18).

showing diffusant streaming out of the capillary from below the capillary mouth, is shown in Figure 2.

Nanis et al. (15) give the magnitude of the $\Delta \ell$ -region as a function of stirring rate. Calculation of a Reynold's Number (N_{Re}) was based on the rotation rate of the capillary (ω), the radius of the rotating arm (r), the kinematic viscosity (ν), and the inside diameter of the capillary (d), leading to the following expression:

$$N_{Re} = 2\pi r \omega d / \nu \quad (2.1)$$

Against the Reynold's Number they plotted a dimensionless $\Delta \ell$; that is, $\Delta \ell$ divided by the internal diameter of the capillary (d). This plot, shown in Figure 3, indicates that $\Delta \ell/d$ increases with stirring rate, approaching a value of unity at large N_{Re} . The solid curve of Figure 3 is an approximation which fits the data at low Reynold's Numbers (less than 10). This approximation may be expressed as:

$$\Delta \ell/d = 0.17N_{Re} - 0.013N_{Re}^2 + 0.00055N_{Re}^3 \quad (2.2)$$

Experiments at high Reynold's Numbers ($Re \geq 100$) were done with liquid metals (19) and, when combined with the data in Figure 3, suggest a value of $\Delta \ell/d$ approaching zero at low Reynold's Numbers. Because of

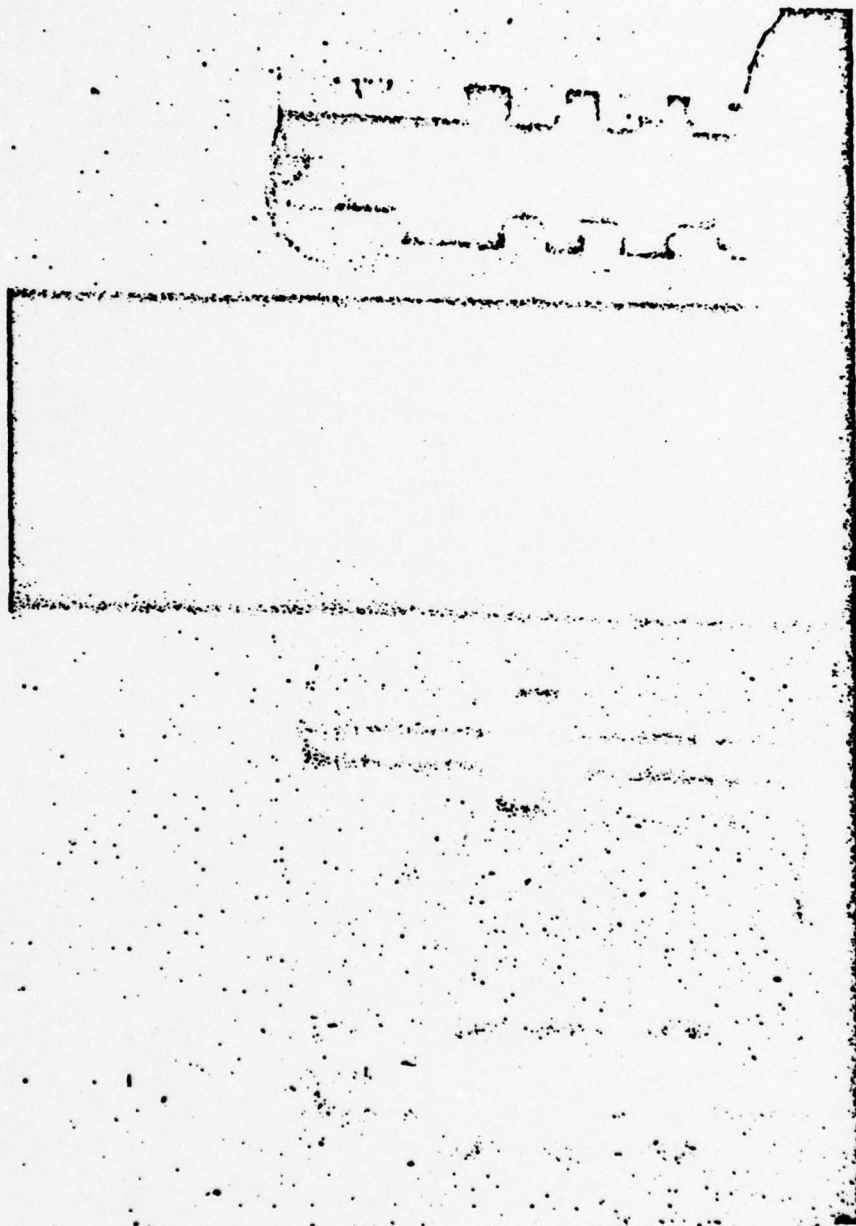


Figure 2. Photograph of KMnO_4 diffusing into water in a stirred-reservoir system (15). The effect of the stirring can be easily seen in the capillary on the right (in focus).

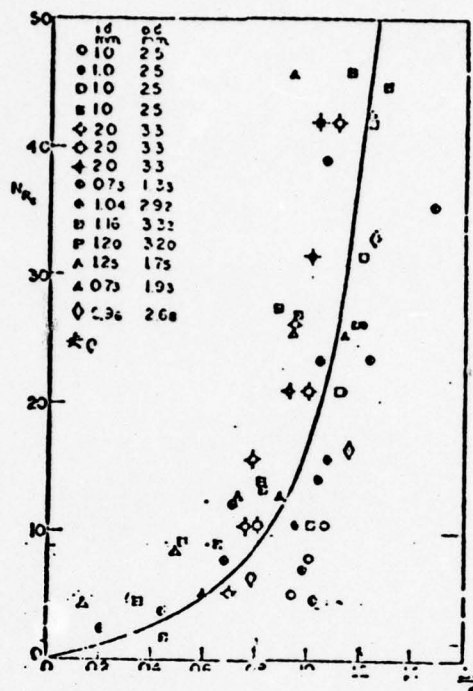


Figure 3. Plot of Reynolds Number against $\Delta l/d$ for various sizes of capillaries. (15)

the small number of data points for very high Reynold's Numbers, no significant statement can be made about the $\Delta \ell$ -effect in that region. In that study, however, a relationship was suggested between $\Delta \ell$ and N_{Re} that could be used as a guide in estimating the expected error in diffusivity calculations due to the $\Delta \ell$ -effect:

$$N_{Re} = 12 \left(\frac{\Delta \ell}{d} \right) \quad (2.3)$$

Previous experimentation with the $\Delta \ell$ -effect (20) has implied that the magnitude of the $\Delta \ell$ -region may be time-dependent. Experiments were done for long times (several days) and for short times (a few hours), all other variables held constant, with the result that the apparent diffusivity for short-time experiments was consistently higher than the apparent diffusivity for long-time experiments. This is probably due to the effect of the $\Delta \ell$ -region growing with time until it reaches a constant value, after which the diffusion effect becomes dominant and the apparent $\Delta \ell$ -effect less significant. The implication of this is that by increasing diffusion time in a stirred-reservoir experiment, the error due to the $\Delta \ell$ -effect is minimized. This follows an earlier suggestion made by Richards (21).

If, in the analysis of capillary experiments

with stirring of the reservoir, the Δl -effect is neglected, the actual length of capillary in which diffusion-only occurs will be shorter than the actual length of the capillary, and therefore, the calculated diffusion coefficient will appear larger than should be expected.'

(b). The No-Stirring Model

In order for there not to be a " Δl -effect", there can be no stirring of the reservoir solution outside the capillary. If the reservoir material is not stirred, however, the capillary-reservoir interface cannot be maintained at zero diffusant concentration. Because of the complexities of solution of the diffusion equation with a changing boundary condition, experimental results based on the no-stirring model were not reported until a computer-simulated mathematical model was developed (22). The experiments described above, all done in the 1950's and 1960's, were based on the stirring model of capillary diffusion.'

B. Existing Diffusivity Data

1. Potassium Chloride (KCl)

The limiting value of the diffusivity of KCl

(that is, infinite dilution) is given as $1.99 \times 10^{-5} \text{ cm}^2/\text{sec}$ at 25°C (23). The minimum value is given as 1.835×10^{-5} at 0.2 molar concentration; the diffusivity then increases with increasing concentration. At 1.0 molar KCl, the diffusion coefficient is $1.893 \times 10^{-5} \text{ cm}^2/\text{sec}$. C.Y. Luk integrated the data described above to obtain an average (integral) diffusion coefficient for 1.0 molar KCl diffusing into pure water at 25°C of $1.866 \times 10^{-5} \text{ cm}^2/\text{sec}$. (20)

As this value is generally accepted as valid, it was considered to be a good starting point to do no-stirring diffusion experiments with 1.0 molar KCl in water at 25°C and to compare the results with the value listed above.

2. Zinc Oxide (ZnO)

The system under consideration is 0.01 molar zinc oxide in 40% (wt.) potassium hydroxide, diffusing into 40% KOH at 25°C . This electrolyte mixture is of particular interest to electrochemical engineers, as it is commonly used in battery systems. Data have been published (24) for the diffusion coefficient of 0.01 molar ZnO in 23.4% KOH as $7.10 \times 10^{-6} \text{ cm}^2/\text{sec}$, along with values for other concentrations of zincate ion.

3. Cupric Sulfate (CuSO_4)

There has been one generally accepted "standard" set of values for diffusion coefficients for cupric sulfate/sulfuric acid aqueous solutions (25). These data have been around for about forty years, and have formed the basis of most experiments done in that time for which these diffusivities are required. The values obtained from these experiments by Cole and Gordon, shown in Table 2.1, were obtained by a diaphragm cell technique, and were run at 18°C .

A more recent study by Eversole (26) gives data for low concentrations of cupric sulfate diffusing in water at 25°C (see Table 2.2). Both these data and that of Cole and Gordon (Table 2.1) indicate a concentration-dependence of the diffusion coefficient. Yet, as discussed later in section III-A, the solution of Fick's 2nd Law of Diffusion (the "diffusion equation") is based on the assumption of constant diffusivity. It may be argued, though, that the change in diffusivity with respect to concentration change is small enough to make that assumption reasonable at low concentrations. This paradox will be discussed at the end of this report, in the light of the data in Tables 2.1 and 2.2, as well as the present study.

Table 2.1 - Data of Cole and Gordon (25)
for $\text{CuSO}_4/\text{H}_2\text{SO}_4$ solutions diffusing
into H_2SO_4 at 18°C .

<u>Molarity of CuSO_4</u>	<u>Molarity of H_2SO_4</u>	<u>$D \times 10^6 \text{ cm}^2/\text{sec}$</u>
0.05	0.00	6.05
0.10	0.00	5.85
0.15	0.00	5.50
0.05	0.50	5.95
0.10	0.50	5.90
0.15	0.50	5.75
0.05	1.80	5.00
0.10	1.80	4.95
0.15	1.80	4.90

Table 2.2 - Data of Eversole et al. (26) for
CuSO₄/H₂O solutions diffusing into
water at 25°C.

<u>Molarity of CuSO₄</u>	<u>$\bar{D} \times 10^6 \text{ cm}^2/\text{sec}$</u>
0.0028	7.474
0.0056	7.159
0.0084	6.922
0.0112	6.726
0.0308	6.159
0.0980	5.644
0.2100	5.349

III. Theoretical Background

A. Solutions of the Diffusion Equation

1. The Diffusion Equation

We are concerned with diffusion of electrolyte out of a capillary into a bulk solution. In the capillary is the electrolyte under study in a solution of supporting electrolyte (water, acid, or base solution). The bulk liquid (surrounding the capillary) is the supporting electrolyte only. Temperature is assumed constant in and around the capillary; therefore, thermal effects are assumed non-existent. Diffusion within the capillary is assumed to be one-dimensional. The governing diffusion equation is known as Fick's Second Law of Diffusion:

$$\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2} \quad (3.1)$$

where,

c = concentration of diffusant in capillary

t = time

x = distance from closed end of capillary

D = diffusion coefficient

For convenience in later discussion, the following dimensionless parameters are introduced:

$$\phi = c/c_0 \quad (c_0 = \text{initial conc. in capillary})$$

$$\lambda = x/L \quad (L = \text{length of capillary})$$

$$\tau = t/L^2$$

Equation 3.1 may now be rewritten in dimensionless form:

$$\frac{\partial \phi}{\partial \tau} = \frac{\partial^2 \phi}{\partial \lambda^2} \quad (3.2)$$

The initial condition is defined as:

$$\phi = 1 \quad \text{at} \quad 0 \leq \lambda \leq L, \quad \tau = 0 \quad (3.3)$$

Boundary conditions will be determined by whatever is occurring at the interface of the bulk solution and the capillary mouth.

2. Stirring of the Bulk Solution

It has been demonstrated by Luk (20) that a fluid velocity of 2×10^{-4} cm./sec across the capillary mouth is sufficient to maintain a zero-concentration of diffusant at the interface, if the concentration in the capillary is low (i.e., less than one molar for CuSO_4). The method of calculating the bulk fluid velocity (and corresponding Reynold's Number) will be discussed in a later chapter of this report. It may be assumed that this minimum velocity requirement is met, and that there is no diffusing electrolyte outside the capillary mouth.

Thus, the boundary conditions for equation 3.2 are:

$$\frac{\partial \phi}{\partial \lambda} = 0 \quad \text{at} \quad \lambda = 0, \tau > 0 \quad (3.4)$$

$$\phi = 0 \quad \text{at} \quad \lambda = 1, \tau > 0 \quad (3.5)$$

Using the method of "separation of variables", equation 3.2, with conditions 3.3, 3.4, and 3.5 may be solved as:

$$\phi = \frac{8}{\pi^2} \sum_{n=0}^{\infty} \left[\frac{1}{(2n+1)^2} \cdot \text{EXP} \left(-\frac{(2n+1)^2 \pi^2 \tau^2}{4} \right) \right] \quad (3.6)$$

Note that as dimensionless time (τ) increases, the exponential value in parenthesis decreases. For sufficiently long time, all but the first term ($n=0$) may be dropped. At $\tau = 0.10$, for example, neglecting the $n=1$ and higher terms gives a value of ϕ which is 0.01% less than if several terms were included. At $\tau = 0.06$, however, the error due to neglecting higher order terms is -3.4%, and is not considered negligible. It can be shown that for dimensionless time of 0.10 or greater, a single term equation may be used with no appreciable loss of accuracy. It is possible, however, to solve equation 3.2 by other methods, with the goal of finding a solution suitable for use with small dimensionless time. One such solution

is obtained by the method of Laplace Transforms, as shown in equation 3.7:

$$\phi = 1 - \sqrt{\frac{4\tau}{\pi}} \left[1 + 2 \sum_{n=1}^{\infty} (-1)^n \left(\frac{e^{-n^2/\tau}}{\pi} - \frac{n}{\tau} \operatorname{erfc} \frac{n}{\tau} \right) \right] \quad (3.7)$$

In this case, it can be shown that the entire summation term may be dropped for small dimensionless time (≤ 0.06). Thus, for capillary diffusion with stirring at the capillary mouth, the following two equations are valid in the specified ranges of dimensionless time:

$$\text{For } \tau \geq 0.10, \quad \phi = \frac{8}{\pi^2} \cdot \operatorname{EXP}(-\tau^2 \tau / 4) \quad (3.8)$$

$$\text{For } \tau \leq 0.06, \quad \phi = 1 - (4\tau/\pi)^{1/2} \quad (3.9)$$

For $0.06 \leq \tau \leq 0.10$, several terms of either equation (3.6 or 3.7) may be used. These equations may be rearranged to give τ as a function of ϕ , the dimensionless concentration. Thus, if c_0 is known, capillary length (L) is measured, and diffusion time (t) is specified, it is possible to compute a diffusion coefficient from measurements of average concentration of diffusant remaining in the capillary (c) after the specified diffusion time period.

3.1 Calculation of Δc

As it is the purpose of these experiments to

determine the so-called " $\Delta \ell$ -effect" in stirred-reservoir experiments, as described previously, it will be useful to have a way of calculating the magnitude of $\Delta \ell$. If the equations of the previous section (3.6 through 3.9) are used to calculate a dimensionless time from a measurement of concentration, and if a diffusion coefficient is known (from tabulated values, or from other experiments), then an effective diffusion length (L') may be calculated. L' should be considered to be the length of capillary in which diffusion alone occurs. Since the real length of the capillary is known (L), and the effective length may be calculated (L'), the section of capillary in which non-diffusive mass transport occurs may be calculated as:

$$\Delta \ell = L - L' \quad (3.10)$$

The results of no-stirring experiments, from which a diffusivity may also be calculated, may be used to calculate $\Delta \ell$ in the stirred-reservoir experiments.

4. No-Stirring of the Bulk Solution

The " $\Delta \ell$ -effect" discussed above may be avoided by not stirring the bulk fluid around the capillary. If there is no stirring, however, the zero-concentration boundary condition (equation 3.5) is not valid. In this

case, it is necessary to consider diffusion outside the capillary in three dimensions, and the solution of equation 3.2 is very complicated. A paper entitled "An Improved Model for Capillary Diffusion with No External Stirring" (22) discusses computer modeling of this situation, and resultant numerical solutions. Figure 4 is a reproduction of the plot of ϕ vs. τ from the paper described above. It shows both the analytic solution for the stirring boundary condition (equation 3.6 or 3.7), and the numerical solution for no-stirring. (A third curve shows an analytic solution based on the assumption of one-dimensional diffusion with no stirring, but this appears to differ greatly from the numerical solution for all but very small values of τ).

It may be inferred from Figure 4 that, in the limit of decreasing dimensionless time, the no-stir numerical solution approaches the short-time solution for stirring (equation 3.9). By assuming that the short-time no-stirring approximation will have the same form as equation 3.9, and plotting the data of Figure 4 on a log-log scale, the following

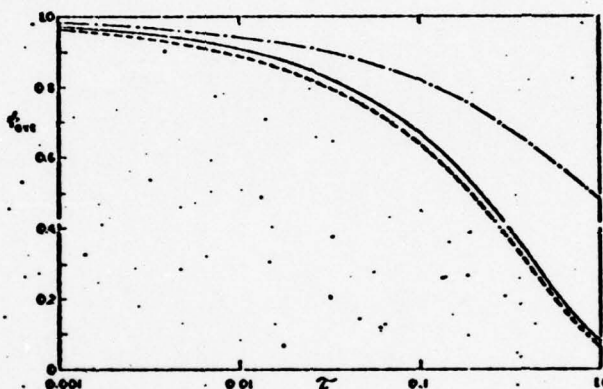


Figure 4. Average capillary concentration (Φ_{ave}) vs. dimensionless time (τ). (22)

- No stir, three dim., computed
- Stirring, one dim., analytic
- · - · - No stir, one dim., analytic

empirical expression is obtained:

$$\phi = 1 - \left(\frac{4\tau}{\pi}\right)^{0.54} \quad ; \quad 0 < \tau < 0.3 \quad (3.11)$$

This equation coincides with the no-stirring numerical solution to less than 1% deviation for the range of dimensionless time listed above. Thus, short-time experiments may be run with no stirring of the bulk solution, and diffusion coefficients may be calculated. (It should be noted that a similar procedure to the above could be used to obtain a long-time approximation for no-stirring experiments, also. All experiments described in this report, however, were run in the short-time range defined above.)

IV. Experimental Apparatus and Procedures

A. Capillaries

Two sets of lucite capillaries were used; one set for the no-stirring experiments, and the other for those experiments during which the reservoir was stirred. For the no-stirring mode, the capillaries used were the same as described by C. Y. Luk in his research thesis (20). Each of the four capillaries looked like the one shown in Figure 5, except for differences in internal length (shaded area in figure, notation "L"). Two of the no-stir capillaries had internal length of one inch (2.54 cm.) and the other two were of 1.375 inch (3.49 cm.) internal length. The internal diameter of each capillary was 1/16 inch (0.158 cm.). The flat plate and collar at the mouth of the capillary (shown in the figure) act to minimize convection caused by diffusant which would fall down the side of the capillary if no collar was present.

The need for the collar is demonstrated in Figures 6a and 6b.⁽²⁰⁾ In Figure 6a, a capillary is initially filled with concentrated KMnO_4 and is placed in a water-filled reservoir. Even without external stirring, the denser-than-water KMnO_4

solution falls over the side of the capillary, creating an undesirable stirring effect. In Figure 6b, the same capillary is shown, this time with a collar-and-barrier arrangement, held in place with black wax. Note that now the diffusing KMnO_4 solution remains in the vicinity of the capillary mouth, as described by the no-stirring boundary conditions. (In the figure, a small amount of KMnO_4 seems to be falling away from the capillary. This is due to a poor seal with the wax. New capillaries were made with the collar an integral part of the whole capillary, and these new capillaries, as shown in Figure 5, were the ones used in the no-stirring experiments.)

For the stirred-reservoir experiments, four new capillaries were made, each 1.0 cm. in internal length and 0.1 cm. internal diameter. These capillaries look like the one shown in Figure 6a. There is no collar on the capillary in this series of experiments, because forced convection is the desired result of stirring the reservoir, unlike the no-stirring model, in which all convection should be eliminated.

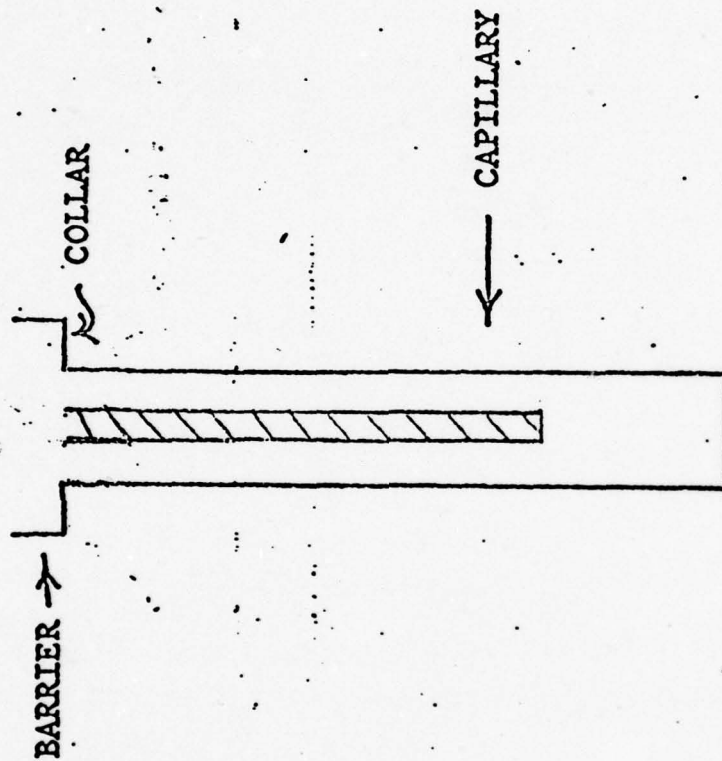


Figure 5 - Drawing (not to scale) of capillary used in no-stirring experiments. Diffusant is in shaded area.

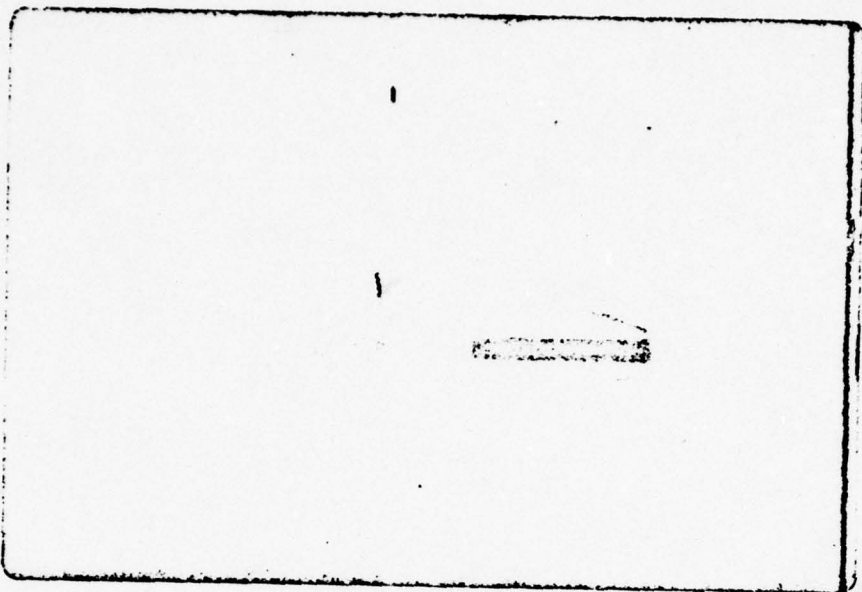


Figure 6a - KMnO_4 -filled capillary
in water reservoir. Note that
 KMnO_4 falls due to convection.

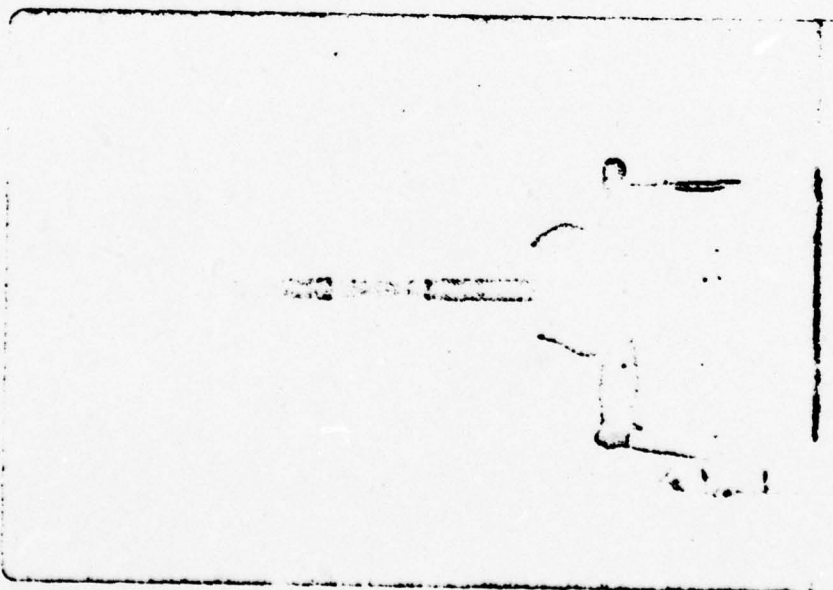


Figure 6b - Same capillary as
at left except that anti-
convection barrier is in place.

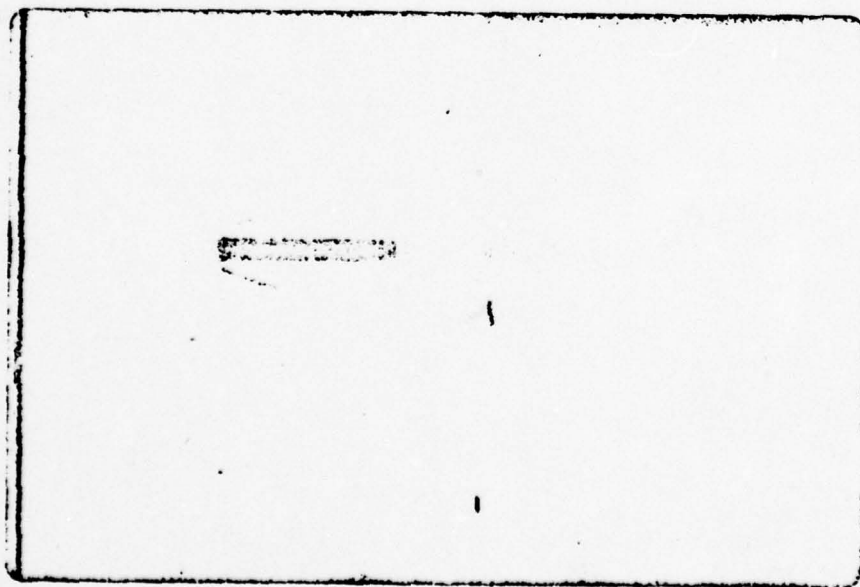


Figure 6a - KMnO_4 -filled capillary in water reservoir. Note that KMnO_4 falls due to convection.

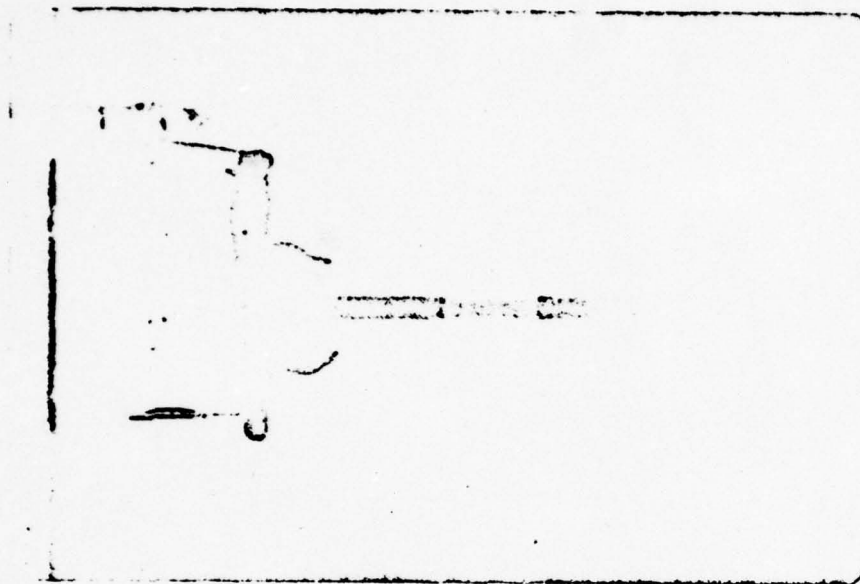


Figure 6b - Same capillary as at left except that anti-convection barrier is in place.

B. Flow-Channel / Reservoir

A rectangular-shaped lucite box was used to hold the capillaries and surrounding reservoir material. The box was designed so that it could be used as a flow-channel for stirred-reservoir experiments or as a static reservoir for the no-stirring experiments. Holes were made in the base of the reservoir box so that up to six capillaries at one time could sit in the reservoir. The outside dimensions of the capillaries and the locations of the six holes were made so as to insure that the top of each capillary would be at the same height and distance from sidewalls as all of the others. This arrangement assures that in the stirred-reservoir experiments, the fluid velocity passing the capillaries would be equal at each capillary-reservoir interface. As shown in the figure, the flow pattern is defined by the geometry of the box, with incoming reservoir fluid entering at the opening labelled "A" and leaving at "B" (see Figure 7). A thermal regulator maintains constant temperature, and a constant-head tank maintains constant flow rate. The overall flow chart is shown in Figure 7 on the next page.

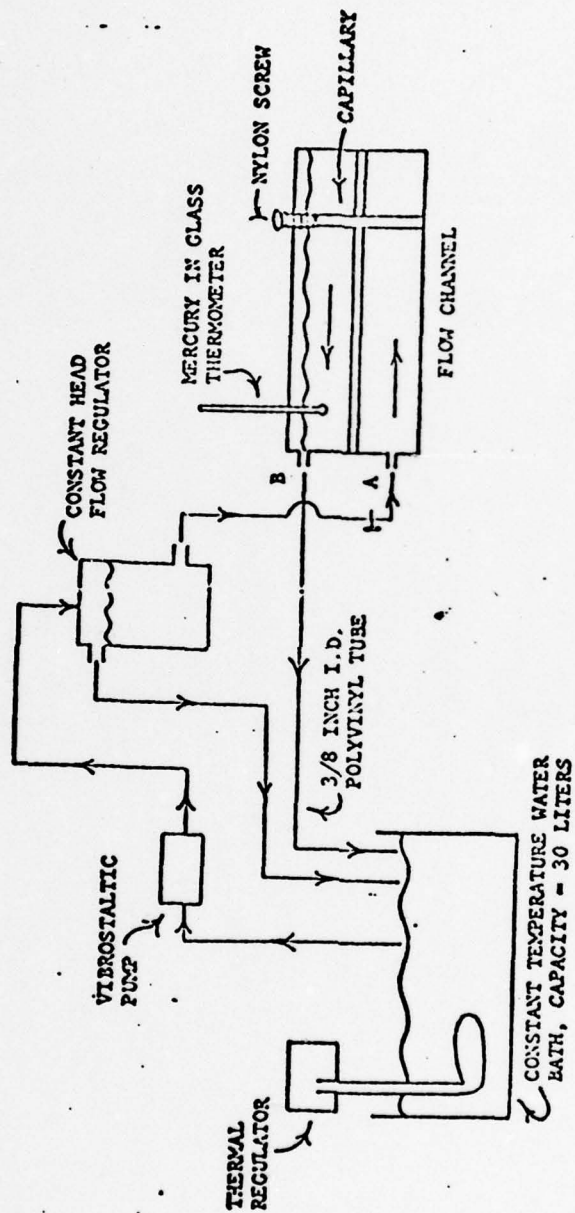


Figure 7 - Flow chart for reservoir fluid in stirring experiments.

The no-stirring experiments do not require such an elaborate flow system as described above. All that is required is a box which holds the capillaries in a static reservoir, all at uniform temperature.

In order to insure a uniform, non-convective start-up of the no-stirring experiments, nylon screws were installed in the top of the reservoir box, located above each capillary. When an experiment was to begin, the diffusant-filled capillary was placed in the partially-filled reservoir box. (The level of the reservoir had to be below the capillary mouth, so that no splashing of the reservoir fluid would remove capillary material.) The top was firmly placed atop the reservoir box, and the nylon screws were tightened, forming a seal at the capillary-reservoir interface. At this time, the reservoir could be filled to the top, and the experiment would begin when the nylon screws were removed, thus exposing the capillaries to the reservoir.

C. Temperature Control

1. Stirring Experiments

As shown in Figure 7 (p. 32), the temperature of the reservoir water is maintained at a predetermined

constant value by a feedback control system. In a thirty-liter holding tank, a temperature regulator maintains constant temperature, with a stirring blade in the tank keeping the water moving. A circulating pump sends the heated water to a two-liter beaker which acts as a constant-head tank, sending water at constant pressure (i.e., constant flow rate) into the reservoir box. Out of the reservoir box, the water is returned to the heating tank.

Temperature is monitored with a copper and constantan (in thin glass tubing) thermocouple, inserted into the reservoir, connected to a millivoltmeter and chart recorder. Two thermocouples were connected in series, with another pair of thermocouples at an ice-and-water (0°C) reference, all read on a Hewlett-Packard digital voltmeter, allowing readings accurate to 0.5°C.

2. No-Stirring Experiments

During those diffusion experiments in which fluid does not flow through the reservoir chamber (that is, no stirring), the temperature of the static reservoir is kept constant by holding the entire reservoir box in a pool of constant temperature water. Thus

the circulating system which maintains constant temperature in the reservoir bath for stirred-reservoir experiments is also used for the no-stirring series, except that the heated water surrounds the box, rather than flowing through it. Again, temperature is monitored throughout the diffusion experiments.

D. Analytical Technique

When a diffusion experiment is finished, each capillary must be removed from the reservoir and its contents analyzed to determine the average concentration of diffusant remaining after the allotted diffusion time. The analytical device used in this determination was a Techtron model AA-120 Atomic Absorption Spectrophotometer (A.A.S.), which utilizes the principle of optical absorption of a specific wavelength corresponding to a specific element, giving a measurement of ionic concentration read on the A.A.S. in the form of "absorbance units" (on an arbitrary zero-to-hundred scale). The recommended range of concentrations to be used with the A.A.S., for the elements of interest in these experiments, was on the order of 10^{-5} molar ion concentration. In order to calibrate the A.A.S., a series of standard solutions, across a concentration

range of 10^{-5} to 10^{-4} molar, was made up for each of the elements to be analyzed (Zn, Cu, K).

In order to analyze the capillary contents after diffusion, it is necessary to reduce the ion concentration to the working range of the A.A.S. This is accomplished by diluting the capillary contents into a known volume of distilled water. When converting from the "absorbance units" readout on the A.A.S. to a molar concentration, this dilution factor is accounted for.

E. Calculation of Capillary Volumes

Capillary volumes were determined by running a "zero-time" experiment; that is, by filling each capillary with diffusant of known ion concentration and immediately emptying and analyzing the contents. If no diffusion was allowed to occur, then the apparent concentration measured on the A.A.S. should agree with the known concentration of diffusant initially in the capillary. Thus the only unknown value is the capillary volume, which may then be calculated directly.

F. Calculation of Reynold's Number (Stirring Experiments)

Fluid velocities were calculated by assuming

laminar flow in the flow channel, with known geometry. The velocity profile in the horizontal direction is given by equation 4.1 below, with V_c , the centerline velocity, described by equation 4.2 .

$$V(y,z) = V_c \left[1 - (2y/w)^2 \right] \quad (4.1)$$

$$V_c = V_t \left[1 - (z/D)^2 \right] \quad (4.2)$$

where, V_c = centerline velocity, cm/sec
 V_t = surface velocity above centerline
 w = channel width, cm
 D = water depth in channel, cm
 y = horizontal distance from centerline, cm
 z = vertical distance from centerline, cm

The average velocity in the flow channel, \bar{V} , is based on V_t and the assumption of laminar flow, as given by equation 4.3. This average velocity may also be expressed as the ratio of volumetric flow through the channel (Q) to the cross-sectional area of flow (A):

$$V_t = 9/4 \bar{V} = 9/4 \cdot Q/A \quad (4.3)$$

The following values have been measured in the flow channel: The capillaries are located at $y = \pm 0.7$, $z = 0.5$. The dimensions of the channel are such that: $w = 4.6$, $D = 1.8$. Insertion of

these values into equations 4.1, 4.2, and 4.3 gives rise to the following expression for $V(y,z)$ as a function of flow rate (Q) for this known geometry:

$$V(y,z) = 0.2275 Q \quad (4.4)$$

Thus, the Reynold's Number at the capillary mouth may be calculated from a measured flow rate, according to the following formula:

$$N_{Re} = \frac{0.2275 d \rho Q}{\mu} \quad (4.5)$$

in which:

d = capillary inside diameter, cm

ρ = density of reservoir fluid, gm/cm³

Q = reservoir flow rate, cm³/sec

μ = reservoir fluid viscosity, poise

G. Experimental Procedure

1. No-Stirring Experiment

- a. Fill reservoir partly (about 75% full)
- b. Place reservoir box in constant-temperature bath; wait until internal temperature reaches steady-state.
- c. Fill the capillaries with diffusant, using a sterile hypodermic needle for each.
- d. Insert capillaries into reservoir box and close box. Seal tops with nylon screws.

- e. Fill reservoir completely; wait again for temperature to stabilize.
- f. To initiate diffusion, slowly turn the nylon screws until each is as high as it can go without coming out of the box. The capillary-reservoir interface is now free of obstruction and diffusion will proceed until the screws are tightened down.
- g. After diffusion is stopped (nylon screws back in place) and time is noted, empty the reservoir box of fluid, by removing the box from the constant-temperature bath, and opening one of the holes in the side of the box, allowing reservoir fluid to drain out.
- h. When the level of the reservoir material is well below that of the capillary tops, remove the top of the reservoir box and then remove each of the capillaries from the reservoir.
- i. Using a fresh, sterile hypodermic needle (use a fresh one for each capillary), remove the capillary's contents and place in a volumetric flask. Fill the volumetric

flask up to the mark, first with the washings of the capillary (wash several times with water) and then with water for the remainder. The capillary contents have now been removed and diluted to a known volume, as described earlier in this section (see p. 36).

- j. Proceed with analysis on the A.A.S., to obtain a measured value of average concentration of ion remaining in the capillary after diffusion. This value, divided by the initial ion concentration, is ϕ , and may be used in the appropriate equation found on pp. 21-22 to find a diffusion coefficient.

2. Stirred-Reservoir Experiment

- a. Fill reservoir and start flow system.
Allow temperature to stabilize.
- b. Periodically check flow rate both before and during experiment.
- c. Fill capillaries with diffusant, using a sterile hypodermic needle.
- d. Insert capillaries in reservoir, noting time.
- e. After desired diffusion time is passed, remove capillaries from flow channel.
- f. Continue steps "i" and "j" from above.

V. Experimental Results

A. No-Stirring Experiments

1. Potassium Chloride in Water

The initial no-stirring diffusion experiment involved 1.0M KCl in H_2O diffusing into H_2O in a static reservoir at a temperature of $25^{\circ}C$. Using four capillaries with the anti-convection collars, the results listed in Table 5.1 were obtained. As shown, the average diffusion coefficient of the four data points is: $1.843 \times 10^{-5} \text{ cm}^2/\text{sec}$. The standard deviation is 0.183×10^{-5} .

2. Zinc Oxide in Potassium Hydroxide

A series of diffusion experiments were run in which 0.01 molar ZnO in 40% (by weight) KOH diffused into 40% KOH at $25^{\circ}C$, in a non-stirred reservoir. The results of these experiments, two series of four capillaries, are listed in Table 5.2, showing an average diffusivity of $6.45 \times 10^{-6} \text{ cm}^2/\text{sec}$, and a standard deviation of 2.42×10^{-6} . The tabulated data is listed in two groups, according to the length of the capillary.

3. Cupric Sulfate in Water

Table 5.3 shows the results of experiments in which 0.05 molar CuSO_4 in aqueous solution diffusing into static H_2O at 25°C . Again, the data are divided into two groups according to capillary length. As indicated, the average diffusion coefficient for the eight tabulated values is $5.560 \times 10^{-6} \text{ cm}^2/\text{sec}$, with a standard deviation of 2.066×10^{-6} .

4. Cupric Sulfate in Sulfuric Acid

The $\text{CuSO}_4/\text{H}_2\text{SO}_4$ system was studied over a range of cupric ion concentrations and at two temperatures. Cupric sulfate, in a solution of half-molar sulfuric acid, diffused for 24 hours in a static reservoir of $0.5\text{M H}_2\text{SO}_4$. At 25°C , cupric concentrations of 0.005M , 0.02M , 0.05M , and 0.10M were studied. At 35.5°C , the CuSO_4 concentrations were 0.005M , 0.05M , and 0.10M . For each temperature and concentration, Table 5.4 lists the number of experimental data points ("N"), the concentration, temperature, average diffusion coefficient, and standard deviation.

B. Stirred-Reservoir Experiments

In the experiments in which the reservoir was stirred, an aqueous solution of 0.05 molar CuSO_4 at 26°C initially filled the capillaries, which sat in a reservoir of flowing H_2O . Two sets of experiments were run: one at a flow rate of 0.817 ml/sec ($N_{\text{Re}} = 2.03$) and the other at 2.915 ml/sec ($N_{\text{Re}} = 7.55$). In each series, several diffusion runs were made, with the diffusion times varying from two to twenty-four hours.

Table 5.5 is a summary of these experiments, showing for each flow rate and diffusion time, the average diffusion coefficient, the standard deviation, and the number of data points.

TABLE 5.1 - Experimental Results for 1.0 Molar KCl
in H₂O diffusing into H₂O.

<u>L. cm.</u>	<u>t. hrs.</u>	$\frac{C_{ave}}{C_0}$	<u>γ</u>	<u>$\bar{D} \times 10^5 \text{ cm}^2/\text{sec}$</u>
2.54	24.0	0.481	0.2546	1.901
2.54	24.0	0.484	0.2515	1.878
3.49	24.0	0.644	0.1122	1.582
3.49	24.0	0.605	0.1427	2.011

Reservoir not stirred.

Capillary internal diameter: 0.158 cm.

Reservoir temperature: 25.0 ± 0.5 °C.

$$\bar{D}_{avg.} = 1.843 \times 10^{-5} \text{ cm}^2/\text{sec}$$

$$\text{Standard Deviation} = 0.183 \times 10^{-5} \text{ cm}^2/\text{sec}$$

$$95\% \text{ confidence limits: } 1.73 \leq \bar{D} \leq 1.95 \text{ (} \times 10^{-5} \text{)}$$

TABLE 5.2 - Experimental Results for 0.01 Molar ZnO
in 40% (wt.) KOH diffusing into KOH.

<u>L, cm.</u>	<u>t, hrs.</u>	$\frac{C_{ave}}{C_0}$	γ	$\bar{D} \times 10^6 \text{ cm}^2/\text{sec}$
2.54	23.0	0.6764	0.0986	7.68
2.54	23.0	0.7089	0.0811	6.32
2.54	24.5	0.8877	0.0141	1.04
2.54	24.5	0.7089	0.0811	5.93
3.49	23.0	0.7361	0.0677	9.95
3.49	23.0	0.7475	0.0624	9.17
3.49	24.5	0.7655	0.0545	7.68
3.49	24.5	0.8373	0.0278	3.84

Reservoir not stirred.

Capillary internal diameter: 0.158 cm.

Reservoir temperature: 25.0 ± 0.5 °C.

$$\bar{D}_{avg.} = 6.45 \times 10^{-6} \text{ cm}^2/\text{sec}$$

$$\text{Standard deviation} = 2.90 \times 10^{-6} \text{ cm}^2/\text{sec}$$

$$95\% \text{ confidence limits: } 4.03 \leq \bar{D} \leq 8.87 \text{ (} \times 10^{-6} \text{)}$$

TABLE 5.3 - Experimental Results for 0.05 Molar CuSO_4
in H_2O Diffusing into H_2O .

<u>L, cm.</u>	<u>t, hrs.</u>	$\frac{C_{ave}}{C_0}$	γ	$\bar{D} \times 10^6 \text{ cm}^2/\text{sec}$
2.54	22.5	0.7695	0.0420	3.344
2.54	22.5	0.6305	0.1258	10.020
2.54	24.0	0.7025	0.0844	6.303
2.54	24.0	0.7021	0.0846	6.321
3.49	22.5	0.8328	0.0292	4.396
3.49	22.5	0.8327	0.0293	4.398
3.49	24.0	0.8105	0.0368	5.191
3.49	24.0	0.8244	0.0319	4.510

Reservoir not stirred.

Capillary internal diameter: 0.158 cm.

Reservoir temperature: 25.0 ± 0.5 °C.

$$\bar{D}_{avg.} = 5.560 \times 10^{-6} \text{ cm}^2/\text{sec}$$

$$\text{Standard deviation} = 2.066 \times 10^{-6} \text{ cm}^2/\text{sec}$$

$$95\% \text{ confidence limits: } 4.08 \leq \bar{D} \leq 7.04 \text{ (} \times 10^{-6} \text{)}$$

TABLE 5.4 - Experimental Results for CuSO_4 in 0.5M H_2SO_4
Diffusing into 0.5 Molar H_2SO_4 .

<u>N</u>	<u>C₀ (molar)</u>	<u>T, °C</u>	<u>$\bar{D}_{\text{avg}} \times 10^6 \text{ cm}^2/\text{sec}$</u>	<u>std. dev.</u>
10	0.005	25.0	7.24	0.29
7	0.02	25.0	6.12	0.29
9	0.05	25.0	6.04	0.13
12	0.10	25.0	4.32	0.10
6	0.005	35.5	7.63	1.13
9	0.05	35.5	6.92	0.36
8	0.02	35.5	6.92	0.13

Reservoir not stirred.

Capillary internal diameter: 0.158 cm.

Capillary lengths: 2.54 cm., 3.49 cm. (mixed)

Reservoir temperature: as above, $\pm 0.5^\circ\text{C}$.

N = number of data points represented

C₀ = initial concentration of CuSO_4 in capillary

TABLE 5.5 - Experimental Results for 0.05 Molar CuSO_4
in Water Diffusing into Flowing Water.

<u>N</u>	<u>N_{Re}</u>	<u>Time, hrs.</u>	<u>$\bar{D}_{\text{avg}} \times 10^6 \text{ cm}^2/\text{sec}$</u>	<u>std. dev.</u>
8	2.0	2	7.877	0.47
7	2.0	3	6.317	1.07
4	2.0	10	6.453	0.13
8	2.0	18	5.763	0.62
7	2.0	24	6.088	0.07
4	7.6	2	6.699	0.67
4	7.6	3	7.866	0.31
4	7.6	9	4.746	0.47
4	7.6	18	5.488	0.05
4	7.6	24	5.520	0.03

Reservoir stirred , Reynold's Number given above.

Capillary internal diameter: 0.100 cm.

Capillary length: 1.0 cm.

Reservoir temperature: 26.0 ± 1.0 °C.

N = number of data points represented

VI. Discussion of Data

A. No-Stirring Experiments

1. Potassium Chloride in Water

The data in Table 5.1 represent one diffusion experiment in which four capillaries, each filled with a one-molar solution of KCl in distilled water, sat in a 25° water reservoir for 24 hours, with no external stirring of the reservoir. The mean diffusion coefficient of the four capillaries, found by summing the four individual values and dividing by the number of data points (4) is:

$\bar{D} = 1.843 \times 10^{-5} \text{ cm}^2/\text{sec.}$ The standard deviation of the data is 0.183. According to a double-tailed t-test of significance at the 0.95 confidence level, for four data points (see Appendix C for examples of this type of calculation), any value of \bar{D} such that $1.73 \leq \bar{D} \leq 1.95$ is considered in good agreement with the experimental data of Table 5.1.

As discussed in section II-B, the accepted value for the integral diffusivity of 1M KCl in water at 25°C. is $1.866 \times 10^{-5} \text{ cm}^2/\text{sec.}$, which is in excellent agreement with the above. In addition, C.Y. Luk (20) found values of $1.86 \leq \bar{D} \leq 1.89$ in his experiments with

the same system. The 95% confidence interval of Luk's data appears narrower than that given in the paragraph above for this study, because Luk had 36 experimental data points to evaluate, whereas only four data points are included in this study.

The potassium chloride experiment was intended as an evaluation of this technique, to insure that all equipment was in working order, and that the revised analytical technique (see pp. 23-26) was valid. As the results of this experiment were in such good agreement with previous experimental work as well as the generally "accepted" value, it was decided to continue with this method for zincate and cupric ion diffusivities.

2. Zinc Oxide in Potassium Hydroxide

The data in Table 5.2 represent two diffusion experiments (4 capillaries in each run) in which a solution of 0.01M ZnO in 40% KOH diffused into a static reservoir of 40% KOH. The mean diffusion coefficient and the 95% confidence limits of the data are:

$$\bar{D}_{avg.} = 6.45 \pm 2.42 \times 10^{-6} \text{ cm}^2/\text{sec}$$

Note that one point in Table 5.2 lies outside of

this limit (at $\bar{D} = 1.04 \times 10^{-6}$). Further, as this point is even outside the 99% confidence interval of the data, it may be neglected, and a new mean value calculated. The new mean (of the seven remaining points) and corresponding 95% confidence limits are:

$$\bar{D}_{\text{avg.}} = 7.22 \pm 1.90 \times 10^{-6} \text{ cm}^2/\text{sec}$$

As the range of the scatter is narrower when the extraneous point is not included, the standard deviation is lower and the limits of confidence are reduced.

This diffusion coefficient of 0.01M ZnO in 40% KOH may be compared with the data of Lu (24) (as described in section II-B-2). He studied the system of 0.01M ZnO in 23.4% KOH and found a diffusion coefficient of $7.10 \times 10^{-6} \text{ cm}^2/\text{sec}$ (no range of error reported). According to a double-tailed t-test of significance, within 95% confidence limits, there is no difference between Lu's value and the average diffusion coefficient found in this study. The Stokes-Einstein Equation (below), however, implies that the two diffusivities should be different:

$$D = \frac{RT}{K} \cdot \frac{1}{6\pi r u} \quad (6.1)$$

where, D = diffusion coefficient, cm^2/sec

R = gas constant, $\text{cal}/\text{gm.mole}^\circ\text{K}$

T = absolute temperature, $^\circ\text{K}$

r = ionic radius, \AA

u = viscosity, of medium, cp.

$K = 6.02 \times 10^{23}$ (Avogadro's Number)

The textbook "Alkaline Storage Batteries" (28) gives the viscosity of 40% KOH solutions as 3.5 centipoise and of 23.4% solutions as 1.8 centipoise. If this is so, and all other factors in equation 6.1 are constant, then the expected diffusivity of zincate in 40% KOH should be roughly half of that of the same zincate concentration in 23.4% KOH. As it turns out, there is no significant difference between the two experimentally-determined values within 95% confidence limits. Possible explanations of this are: ionic effects (caused by increase in pH corresponding to higher concentration of KOH, possibly affecting the value of " r " in equation 6.1); and temperature differences (Lu states in his report only that the experiments were run at "room temperature", which could mean anything in the range of 20-25°C.).

C.Y. Luk (20) also studied the 0.01M ZnO in 40% KOH system and found a diffusion coefficient, expressed in terms of his 95% confidence interval as $6.00 \times 10^{-6} \leq D \leq 6.68 \times 10^{-6}$, which (according to the double-tailed t-test at $P = 0.05$) is not different from the data obtained in this study.

The data for the ZnO/KOH system were also studied in order to evaluate any relationship between capillary length and apparent diffusion coefficient in the no-stirring experiment. A double-tailed t-test of significance at $P = 0.05$ showed no difference between the two groups of data (at $L = 3.49$ and $L = 2.54$ cm.), indicating no variation in D of this series of experiments due to capillary length.

3. Cupric Sulfate in Water

The data in Table 5.3 were evaluated in the same manner as described above for KCl and ZnO/KOH. The mean diffusion coefficient was found to be:

$$D_{\text{avg.}} = 5.56 \pm 1.48 \times 10^{-6} \text{ cm}^2/\text{sec}$$

(expressed with 95% confidence limits). One point in the table (at $D = 10.02 \times 10^{-6}$) is outside the 99% confidence interval, and may be discarded. This

lowers the mean value of \bar{D} and reduces the scatter:

$$\bar{D}_{\text{avg.}} = 4.923 \pm 0.968 \times 10^{-6} \text{ cm}^2/\text{sec}$$

As explained in section II-B-3, the data of Eversole et al. (26) represent point values of diffusivities across a large range of concentrations (0 to 0.35 molar). These values, often called the "differential diffusion coefficients" must be integrated as a function of concentration to obtain the integral diffusivity, which is the type of diffusion coefficient obtained by the capillary method. Eversole et al. suggest a relationship of the form: $\bar{D} = a + bC_0^{\frac{1}{2}}$, for less than .35M CuSO_4 in water. In the range of concentrations of interest in this study (C_0 0.05M), the diffusivity may be approximated as a linear function of concentration with no worse than 2% deviation from Eversole's data. The data of Eversole et al. was graphically integrated according to the following formula:

$$\bar{D}_{\text{int.}} = \frac{1}{C_n} \sum_{i=0}^n \bar{D}_i \Delta C_i \quad (6.2)$$

where $\bar{D}_{\text{int.}}$ = integral diffusivity at $C = C_n$

C_i = concentration of CuSO_4 ($C_n = 0.05 \text{ M}$)

\bar{D}_i = point-value of \bar{D} from tabulated values
by Eversole et al., range C_i to C_{i+1} .

This graphical integration of the data from $C_i = 0$ to $C_i = C_n = 0.05$ molar gives a value for the integral diffusivity of cupric sulfate in water at 25° of 5.85×10^{-6} cm²/sec. According to a double-tailed t-test of significance at $P = 0.05$, this value is in good agreement with the experimentally-obtained data shown in Table 5.3.

4. Cupric Sulfate in Sulfuric Acid

Each value of \bar{X} listed in Table 5.4 is an average of a number of individual data points. There are two groups of numbers; four values representing a total of 38 experiments at 25.0°C, and three average values representing a total of 23 data points taken at 35.5°C. Each mean value in the table is listed with the standard deviation. Each group of values at one temperature were evaluated to determine the effect of concentration on the diffusion coefficient. A linear regression of the 38 points at 25°C, with $X = \text{concentration}$ and $Y = \text{diffusivity} \times 10^6$, produced the following linear equation: $Y = -12.812X + 6.017$. However, an F-test of significance at the 0.95 confidence level with 36 degrees of freedom indicates no correlation of the data. Within the 95% limits as

described, slope of the linear regression could be anything from -28.504 to +2.830. As that range includes the slope of zero, which corresponds to no concentration effect, no statement may be made to the effect that diffusivity is a linear function of concentration, based on these experiments.

Similarly, for the 23 points at 35.5°C, a linear regression gives a line of the form: $Y = -4.157X + 7.205$. Again, within the limits of the 95% confidence level, the upper and lower bounds of the slopes of the regression line are, respectively, 16.732 and -25.046, crossing the X-axis.

Following the suggestion of Eversole et al. (26) that the diffusion coefficient may be a function of the square root of molar concentration, the linear regressions were repeated, this time with $X = (C_0)^{\frac{1}{2}}$ and Y as before. Now, the F-test of the data shows correlation between X and Y at the 0.95 confidence level. The upper and lower bounds on the slope of the regression line do not cross the axis, thus indicating a real concentration effect. The best line through the data is: $Y = -7.191X + 6.944$, with the upper and lower

- 21 -

bounds on the slope at: -1.839 and -12.544 , respectively. (The square-root relationship could not be demonstrated with the 35.5° data; this is probably due to greater scatter of data and a smaller number of points to evaluate). As shown in Figure 8, the diffusion coefficient of low-concentrations of CuSO_4 in H_2O is a weak function of concentration. This means that, for low concentrations, it may be justifiable to neglect concentration effects when approximating the diffusion coefficient. As stated earlier, in the discussion of the diffusion equation, it is assumed in Fick's First Law of Diffusion, as treated in this study (see section III), that the diffusion coefficient is constant with respect to time, distance, and concentration. These experiments indicate that that assumption is justified in this range of concentrations.

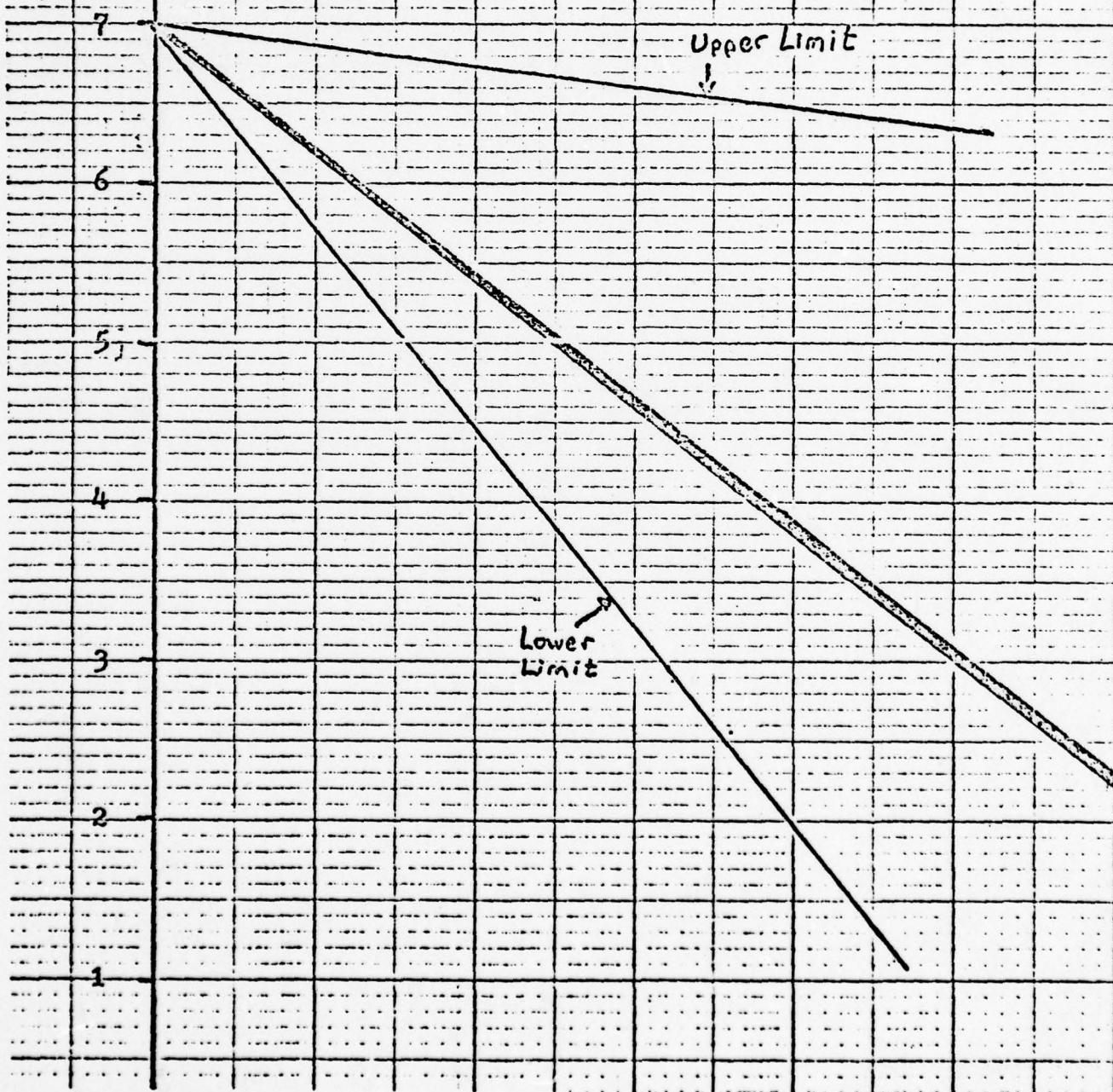
The assumption of constant diffusivity with concentration allows the calculation of a mean diffusion coefficient of all data points at each temperature. Of the 38 experiments at 25.0°C , in the concentration range $0.005 \leq C_0 \leq 0.10$, a mean diffusion coefficient of $5.43 \pm 0.59 \times 10^{-6} \text{ cm}^2/\text{sec}$ was calculated (95% confidence interval given).

Figure 8 Concentration effect on

Diffusion coefficient. 0.05M

CuSO_4 in 0.5M H_2SO_4 . $T = 25^\circ\text{C}$.

Bold line (---) represents the mean data. The two narrow lines represent upper and lower limits of the 95% confidence interval.



- 59 -

In the same concentration range, the 23 data points taken at 35.5°C lead to a mean diffusion coefficient of $6.675 \pm 0.97 \times 10^{-6} \text{ cm}^2/\text{sec}$. The double-tailed t-test of significance shows, even at the 0.98 level of confidence, that the two values are different, suggesting that there is indeed a temperature dependence of the diffusion coefficient, as predicted by the Stokes-Einstein equation.

Figure 9 is a plot of $-\ln(D)$ against temperature for the two mean values discussed above. From this plot, an activation energy of diffusion may be estimated, according to the Boltzmann Equation:

$$D = A \exp (-E_d/RT) \quad (6.3)$$

where, D = diffusion coefficient, cm^2/sec

A = frequency factor, cm^2/sec

E_d = activation energy for diffusion, cal/mole

R = gas constant (1.987 cal/mole-°K)

T = temperature, °K.

The slope of the bold line in Figure 9 corresponds to an activation energy of 0.967 Kcal/mole. The dashed lines represent the upper and lower bounds of the 95% confidence limits on each value, corresponding to values of E_d of, at worst, zero at minimum and 2.096 Kcal/mole maximum. These values are in the

Figure 9

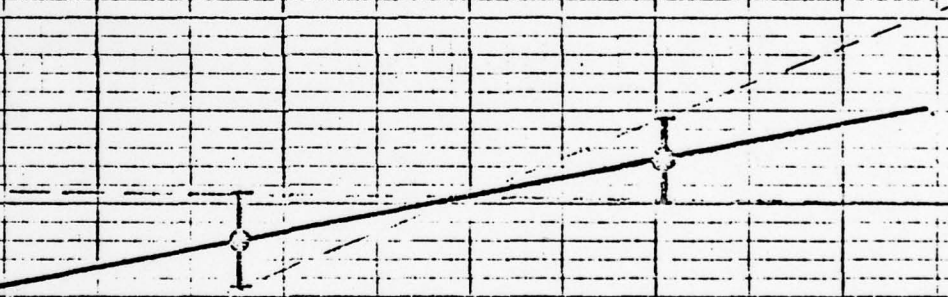
$-\ln \phi$ vs. $1/T$ for
 CuSO_4 in $0.5\text{M H}_2\text{SO}_4$.

$-\ln \phi$

13

12

11



same order of magnitude as values published for similar binary systems (20,24,29).

An interesting aspect of the temperature effect was noted during the initial experimentation with 0.05M CuSO_4 in sulfuric acid. For some unknown reason, the data taken at that concentration led to the calculation of a diffusion coefficient much higher than that of the other CuSO_4 concentrations in the same series. Investigation into the possible cause of this obvious error turned up the fact that during the week in which the 0.05M series was run, the air conditioning had been turned off every night when the building was empty, (this was during the hottest part of the summer) and that the reservoir temperature had climbed almost to 30°C overnight. When the air conditioning system was returned to normal 24-hour operation, the 0.05M series was repeated, and the initial series (with no temperature control) was discarded.

B. Stirred-Reservoir Experiments

In order to evaluate the hydrodynamic effects caused by stirring of the reservoir material, a series of experiments was conducted in which an aqueous

solution of 0.05 molar CuSO_4 diffused into flowing water at 26.0 ± 1.0 °C. The experiments were divided into two groups, as shown in Table 5.5, with one series run at a Reynold's Number (N_{Re}) of 2.03, and the other at $N_{\text{Re}} = 7.55$. In each series, a group of diffusion experiments were run at various diffusion times, from two to twenty-four hours in length. The tabulated data represent the mean and standard deviation of each time and N_{re} experiment.

For each group of values at a given flow rate, a linear regression was run so as to determine the effect of time on the diffusion coefficient. That is, it was desired to know if diffusion time affected the apparent diffusion coefficient, and if so, at what length of time the apparent diffusion coefficient approached the value obtained in no-stirring experiments. Using the variables $X = \text{time}$ and $Y = \text{diffusivity} \times 10^6$, a linear regression of the data at $N_{\text{Re}} \approx 2$ led to the equation: $Y = -0.06X + 6.831$. The mean value of \bar{D} for the whole series (and 95% confidence limits) is $6.146 \pm 0.761 \times 10^{-6} \text{ cm}^2/\text{sec}$. The upper and lower bounds on the slope of the regression line, respectively, are +0.025 and -0.145, indicating that the diffusivity

does not change with diffusion time. Similarly, in the series at $N_{Re} = 7.55$, show no effect of time on diffusivity, as the regression line takes the form $Y = -0.077X + 6.679$. This line is almost identical to the regression line for $N_{Re} = 2.03$. A double-tailed t-test of the two sets of data at two Reynold's Numbers indicates no difference between the two groups at the $P = 0.05$ level. In the no-stirring experiments with $0.05M$ $CuSO_4$ in water at $26^{\circ}C$, the mean value of \bar{D} obtained was $4.923 \pm .968 \times 10^{-6} \text{ cm}^2/\text{sec}$. The t-test indicates that the mean value of all stirred-reservoir experiments, regardless of time or flow rate ($= 6.015 \times 10^{-6}$) is not different from the no-stir value. Interestingly, however, if only the short-time (2 & 3 hour) experiments are considered, at both flow rates, and compared against the no-stir experiment, there is a difference between the two at the 95% confidence level. On the other hand, comparison of the two longest-time experiments (18 & 24 hours) with the no-stir experiment does not show any significant difference.

Thus it may be inferred from the data that

- 54 -

for experiments in which the reservoir is stirred, longer diffusion times approach the values obtained in no-stirring experiments better than the short time experiments. If the so-called " Δl -effect" is significant, then its effect may become negligible if a long enough diffusion time is allowed. However, as long as a reliable technique exists for using the no-stirring model, as has been shown in part A of this section, the stirring model seems impractical for engineering use.

C. Error Analysis

Possible sources of error in the capillary-reservoir technique include: temperature variation, concentration measurement inaccuracy, inexact filling of the reservoir and/or capillary, measurements of time and capillary length and, for the stirred-reservoir system, the Δl -effect and fluctuation in Reynold's Number.

Temperature fluctuation leads to an error which may be approximated by Boltzmann's Equation (equation 6.3), in which D is related to $1/T$, where T is in degrees Kelvin:

$$D = A \exp (-E_d/RT)$$

Using values of $T = 298^{\circ}\text{K}$, $R = 1.987 \text{ cal/gmmole-}^{\circ}\text{K}$, $E_d \approx 1000 \text{ cal/gmmole}$, and a maximum temperature deviation of 0.50°C (this was the worst deviation recorded in any no-stirring experiment), the maximum error in \mathcal{N} is given by:

$$\delta \mathcal{N} = \mathcal{N} (E_d / \delta T) / RT^2 = 0.011 \mathcal{N} \quad (6.4)$$

Thus the maximum error due to temperature fluctuation is about 1.1%, in the no-stirring series of experiments. For the stirred-reservoir experiments, a variation in temperature of $\pm 1^{\circ}\text{C}$ was noted, so that the maximum error in that series would be about 2.2%.

The equations in section III which relate \mathcal{N} to ϕ , the final-to-initial concentration ratio, all have the general form: $\mathcal{N} = \frac{\eta t}{L^2} = f(\phi)$. Thus the error in \mathcal{N} due to the analytical system may be expressed as:

$$\delta \mathcal{N} = \left| \frac{\partial \mathcal{N}}{\partial L} \right| \delta L + \left| \frac{\partial \mathcal{N}}{\partial t} \right| \delta t + \left| \frac{\partial \mathcal{N}}{\partial \phi} \right| \delta \phi \quad (6.5)$$

From the definition of \mathcal{N} , the first two terms of equation 6.5 are simplified and the equation becomes:

$$\delta \mathcal{N} / \mathcal{N} = \frac{2 \delta L}{L} + \frac{\delta t}{t} + \frac{1}{\mathcal{N}} \left| \frac{\partial \mathcal{N}}{\partial \phi} \right| \delta \phi \quad (6.6)$$

The last term of 6.6 will depend on the equation for $\phi = f(\mathcal{N})$ used. The $\delta t / t$ term may be neglected, as diffusion time is carefully controlled - in a typical 24-hour run, a one minute error (the

worst that might be expected) only contributes 0.067% to the total error. The $2\phi L/L$ term is probably not negligible, and is estimated by Luk (20) for the no-stirring capillaries to be, at most, around 3%. For the newly-made 1-cm. capillaries used in the stirred-reservoir experiments, the maximum error (based on Luk's formulation, with $L = 1.0$ rather than $L = 2.54$), is 8%. The last term of equation 6.6 is determined by the choice of equation to be used in the concentration analysis. For the no-stirred experiments, equation 3.11 was used:

$$\phi = 1 - \left(\frac{4\tau}{\pi}\right)^{0.54} \quad (3.11)$$

which may be rearranged as:

$$\phi = \frac{1.27}{4t} (1 - \phi)^{1.852} \quad (6.7)$$

and the last term of equation 6.6 becomes:

$$\frac{1.852}{4t} \cdot (1 - \phi)^{0.852} \delta\phi$$

Using lowest values for short-capillary no-stirring experiments ($t = 24$ hrs., $\tau = 0.235$, $\phi = 0.481$) and allowing for the precision of the A.A.S. at $\pm 1\%$, $\delta\phi = 0.05$, and the error term comes to $\delta\phi = 0.177$.

For the stirred-reservoir system, Luk (20) suggests a "typical" error of about 8%. The maximum error in short time stirred experiments (based on equation 3.9), calculated in the same manner as above, is 16%. For long-time stirred-reservoir experiments, the maximum error due to θ comes out to 8%.

Thus, summing all maximal errors for each series, the following are given:

No-Stirring: max. error = 21.8%

Stirring ($\tau > 0.1$): max. error = 18.2%

Stirring ($\tau < 0.05$): max. error = 24.2%

In all experiments discussed earlier in this section, only the no-stir ZnO/KOH experiments showed scatter beyond the maximum error range. A possible explanation of why this happened may be in the handling of the 40% KOH solution. Because of the danger of handling concentrated base, special clothing and gloves were worn when running these experiments. It is quite possible, and in the view of the author, even likely, that the capillary washing and dilution procedure was not as carefully followed as in the other experiments, which required no special clothing or gloves. Perhaps, in a situation such

as that, which requires special handling, many data points should be taken, so as to minimize the effect of random error in analytical technique.

VII. Conclusions

1. The no-stirring model of the capillary-reservoir technique gives values of diffusion coefficients in line with those predicted in the literature for the three systems studied. It appears to be a useful method of evaluating diffusion coefficients of these and similar binary electrolytes.
2. The stirred-reservoir model of the capillary technique has inherent error due to a hydrodynamic (Δl) effect. With long diffusion time the effect is minimized.
3. Given the two conclusions above, the no-stirring model would seem to be a better choice for a standard laboratory procedure to obtain the integral diffusivities of binary electrolytic solutions, at a given temperature and pressure.
4. Analysis of the variance of data in the $\text{CuSO}_4/\text{H}_2\text{SO}_4$ system showed that the diffusion coefficient may be a weak function (possibly proportional to the square root of C_0 , as suggested by others), but that this dependence may be neglected at low concentrations of CuSO_4 such as were studied in these experiments.

5. The integral diffusivity of aqueous 1M KCl diffusing in water at 25°C was found to be $1.843 \pm 0.113 \times 10^{-5} \text{ cm}^2/\text{sec}$. This value is in good agreement with published data for the same system.
6. The integral diffusivity of 0.01M ZnO in 40% KOH diffusing in 40% KOH solution was measured as $7.22 \pm 1.90 \times 10^{-6} \text{ cm}^2/\text{sec}$ using the no-stir capillary-reservoir technique. Because of the large scatter and small number of data points, no significant difference could be found between this value and that of a similar system using 23% KOH solution, although the Stokes-Einstein equation predicts a difference due to viscosity effects. For this reason it is suggested that future users of this technique allow a sufficient number of data points to minimize scatter.
7. The integral diffusivity of low concentration CuSO_4 in half-molar sulfuric acid, diffusing in 0.5M H_2SO_4 was found to have a significant temperature dependence. At 25.0°C, the value is $5.43 \pm 0.59 \times 10^{-6} \text{ cm}^2/\text{sec}$. At 35.5°C, across the same range of concentrations, the integral diffusivity is $6.675 \times 10^{-6} \text{ cm}^2/\text{sec}$. The range of concentrations studied was 0.005-0.10M.

8. The $\text{CuSO}_4/\text{H}_2\text{O}$ system was studied using both the stirring and no-stirring models of the capillary-reservoir method. The no-stir experimental results gave a value of the integral diffusion coefficient as $4.923 \pm 0.968 \times 10^{-6} \text{ cm}^2/\text{sec}$, in good agreement with published data for the same system. The flow channel experiments, when averaged over a range of diffusion times from two to twenty-four hours, did not show significant difference from the no-stir values (within 95% confidence limits). However, when only diffusion times of three hours or less are considered, the average diffusivity is significantly higher than that found in the no-stir experiments. It is hypothesized that this is due to a hydrodynamic effect which increases the apparent diffusion coefficient due to convection of diffusant out of the capillary. This effect is minimized with long diffusion time.
9. The activation energy for diffusion in the low concentration $\text{CuSO}_4/\text{H}_2\text{SO}_4$ system studied was found to be on the order of 1 Kcal/gm-mole.

VIII. Recommendations

1. The effect of viscosity and pH on the diffusion coefficient may be studied in the ZnO/KOH or $\text{CuSO}_4/\text{H}_2\text{SO}_4$ system as follows: Choose a concentration of primary electrolyte (e.g., .05M ZnO) and a range of supporting electrolyte concentrations (e.g., 0-4M KOH , in $\frac{1}{2}$ -molar increments), and run several no-stir diffusion experiments at each concentration of supporting electrolyte. Then, repeat the series of experiments but without the supporting acid or base electrolyte. Instead, use a neutral-pH viscous medium, across a range of viscosities comparable to the initial series of experiments. Comparison of the two series of experiments will indicate how the apparent diffusivity is affected by acid/base concentration, and by viscosity.
2. It would be interesting to study the feasibility of using the capillary-reservoir technique on binary systems other than electrolytes, such as, for example, toluene/benzene mixtures, biological fluids, etc.

APPENDIX A: Nomenclature

<u>Symbol</u>	<u>Meaning</u>
d	inside diameter of capillary, cm.
t	time, hr. or sec. (as noted)
w	width of flow channel, cm.
x	length vector: distance from bottom of capillary
y	horizontal distance vector, cm.
z	vertical distance vector, cm.
A	cross-sectional area of flow channel, cm^2
C	concentration of diffusant, moles/liter
C_0	initial "C" at start of experiment
C_{ave}	average conc. of diffusant in capillary after allotted diffusion time.
D	depth of water in flow channel, cm.
L	capillary length, cm.
L'	effective diffusion length, cm.
N_{Re}	Reynold's Number
Q	volumetric flow rate, ml./sec.
T	temperature, degrees Celcius
V	velocity, cm./sec.
V_c	centerline velocity, cm./sec.
V_t	surface velocity above centerline, cm./sec.
D	diffusion coefficient, $\text{cm}^2/\text{sec.}$
Δl	non-diffusing region of capillary caused by flow

ρ	density at specified temp. and pressure, gm/sm ³
μ	viscosity at " " " " , poise
τ	dimensionless time (see p. 20)
ϕ	dimensionless concentration ratio (see p. 20)
λ	dimensionless length (see p. 20)
ω	rotation rate

APPENDIX B: Calculation of Optimum Capillary Length

There are two interdependent factors to be considered when choosing the length of the capillary diffusion cell; namely, diffusion time and depth. At the beginning of the diffusion time period, the concentration of diffusant is uniform ($C = C_0$) throughout the cell. After immersion in the stirred reservoir, the interfacial concentration goes to zero and a concentration gradient of diffusant develops along the length of the capillary. As the diffusion progresses, the depth of the gradient increases, until eventually it touches the closed end (bottom) of the capillary.

As explained earlier, the diffusion coefficient is computed on the basis of measurement of diffusant remaining in the capillary after a measured time period. Therefore, error in diffusant concentration measurement results in error in calculated diffusivity. It has been shown (27) that the error in calculated diffusivity associated with a given concentration measurement error is highly dependent on the amount of diffusant remaining in the capillary. For example, if 90% of the initial amount of diffusant present in the capillary remains there after diffusion, a 1% error in concentration measurement corresponds to 11.7% error in the resultant

calculated diffusivity. In a diffusion cell in which 50% of the initially-present diffusant remains, the same 1% error in concentration measurement corresponds to a mere 2% error in calculated diffusivity. In order to reduce this to about 1%, over 70% of the initially-present diffusant would have to be removed.

The stirring experiments were to be run for a broad range of diffusion times, so as to determine the magnitude of the ΔC -region as a function of time. It was considered desirable to have diffusion times no longer than a day, yet allow no worse than a 10% error in calculated diffusivity. (The analytical method of analyzing capillary contents has an inherent 1% uncertainty.) In such a case, a two-hour experiment, a one-centimeter long capillary would just meet this requirement.

A capillary shorter than one cm. would not be practical, as a too-small capillary volume leads to a great error in diffusant removal. That is, the larger the capillary volume, the less significant a spilled drop appears in the analysis. Thus, the optimum practical capillary length for stirred-reservoir experiments, 1 mm. capillary diameter, with 0.05 Molar CuSO_4 in water, would be one centimeter.

APPENDIX C: Sample Calculations

1. Calibration of the A.A.S.

Calibration solutions of CuSO_4 in distilled H_2O were made up, as shown below, and were run on the A.A.S., and readings (on an arbitrary zero-to-100 scale) were recorded:

<u>Conc. of $\text{Cu}^{++} \times 10^5 \text{M}$</u>	<u>A.A.S. Reading</u>
3	36.0
4	46.0
5	56.5
6	67.0

Letting "C" be concentration $\times 10^5 \text{M}$, and "AA" the reading on the A.A.S., a least-squares reduction line through the four points above gives the equation:

$$\text{AA} = 10.35 \cdot \text{C} + 4.80$$

This calibration equation was used to obtain concentration values of ion in solution from readings on the A.A.S.

2. Example of no-stirring model

One no-stirring experiment which was run at the same time as the above calibration, was with 0.05M CuSO_4 in 0.5M H_2SO_4 at 25°C . There were 9 data points taken, but only one is presented here

to illustrate the calculations. One such point was for a 3.49cm. long capillary, initially filled with 0.05M CuSO_4 /acid solution, which had diffused for 24 hours in 0.5M acid. The A.A.S. reading for this capillary, which had been washed, and its contents diluted to 50 ml., was $AA = 64.0$. From the calibration equation on the previous page, the concentration of copper in the diluted sample was $C = 5.7199 \times 10^{-5}$ molar. To obtain a value of ϕ , the final-to-initial concentration ratio, divide C by capillary volume (0.0701 ml), multiply by dilution factor (50 ml), and divide by initial concentration (0.05M):

$$\phi = 0.816$$

As this is a short-time, no-stir experiment, use equation 3.11 to calculate a dimensionless time:

$$\phi = 1 - \left(\frac{4\tau}{\pi} \right)^{0.54} \quad (3.11)$$

Rearrangement of the equation so as to solve for τ gives a value of $\tau = 0.035$. From the definition of τ , we obtain:

$$D = \frac{L^2 \tau}{t} = 4.919 \times 10^{-6} \text{ cm}^2/\text{sec.}$$

3. The stirred-reservoir experiments

The same calibration method was used in these experiments as for the no-stirring series. Likewise, the calculation of concentration ratio, ϕ , was made in the same fashion. The choice of equation to use to calculate τ was based on the value of ϕ calculated. If $\phi \geq 0.72$ (corresponding to $\tau = 0.06$), the short-time approximation, equation 3.9 was used. If $\phi \leq 0.633$ (corresponding to $\tau = 0.10$), the long-time approximation, equation 3.8, was used. For values of ϕ between the limits described above, a five-term expansion of the series solution (eq. 3.6) was solved by Newton's Method. A computer program was written which calculated ϕ , chose the appropriate equation, calculated τ , and from that, computed \bar{D} .

Example: For one capillary, length 1 cm., diffusion time = 24 hours, with 0.05M CuSO_4 in water at 26°C, ϕ was calculated as 0.246. This falls in the category of the long-time approximation, so the equation used was 3.8:

$$\phi = \frac{8}{\pi^2} \cdot \exp(-\pi^2 \tau / 4) \quad (3.11)$$

Rearrangement of the equation, solving for τ , gives a value of $\tau = 0.484$, or $\bar{D} = 5.602 \times 10^{-6} \text{ cm}^2/\text{sec}$.

4. Analysis of Variance of Data

The ZnO/KOH data discussed in section VI-A-2 will be used as an example of the statistical analysis of data. The basic data are found in Table 5.2, on page 45. A prepared program for use in a Hewlett-Packard 9100A programmable desk calculator, program 09100-70801, calculated the mean and standard deviation of each of two input samples, "X", and "Y", and computed the t-statistic for correlation of the two samples.

For example, the program was used to compute the mean and std. deviation of the eight points in Table 5.2. The 95% confidence limits of the data were calculated by multiplying the computed standard deviation by the tabulated t-statistic for 7 degrees of freedom and $P=0.05$ (30). Where N = number of data points ($=8$), $t = 2.365$, and the computed standard deviation is 2.89×10^{-6} , the calculated 95% confidence interval is:

$$\sigma_{95} = s t / \sqrt{N} = 2.42 \times 10^{-6} .$$

The 99% confidence interval was computed in the same manner, except that the t-statistic used was for $P = 0.01$ rather than 0.05. When one data point was

found outside the 99% interval, it was discarded and a new mean was calculated.

To compare two samples of data, the program described above was used to calculate a t-statistic for comparison with tabulated values. For example, in comparing the data of Table 5.2 in terms of capillary length, the data was divided into two groups: sample "X" included points taken with 2.54 cm capillaries and sample "Y" was the 3.49 cm capillary sample. The program computed a t-statistic of 0.61 for the two samples, far less than the tabulated value of 2.57 (for 5 degrees of freedom), thus indicating no difference between the two samples, and, no proof of any effect of capillary length on the diffusion coefficient for these data points.

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